Solving the Mammoth Mountain CO₂ Mystery

N 1990 a forest ranger was almost asphyxiated when he entered a floorless, snow-covered cabin near Mammoth Mountain on the eastern side of the Sierra Nevada. At about the same time, trees began to die in four patches, which over the next several years expanded to cover 30 to 35 hectares (76 to 86 acres). (See figure next page.) At first no one thought to connect the cabin incident with the dead trees. But as scientists riddled out the case of the dying trees, the near-asphyxiation of the forest ranger provided a critical clue.

Researchers from the U.S. Geological Survey (USGS) were the first to study the problem in 1994. U.S. Forest Service biologists helped rule out drought and insect infestation as possible causes for the dead trees. The ranger's asphyxia symptoms prompted the USGS to look at carbon dioxide (CO₂) levels in the soil because high CO₂ concentrations are harmful to plants and animals. The USGS also brought experts from Lawrence Livermore and Lawrence Berkeley National Laboratories to analyze soil gas components.

The USGS took about 100 soil gas samples from various areas around Mammoth Mountain—in the patches of dead and dying trees, at the cabin where the ranger had been so short of breath, near the fumaroles (volcanic gas vent), and in areas of healthy trees. Carbon dioxide concentrations analyzed by a portable gas chromatograph ranged from less than 1% in healthy forest, a typical figure for forest soils, to more than 90% at several locations within tree-kill areas. Where CO_2 concentrations exceeded 30%, most trees were dead. Other lethal agents were not apparent, and the soils showed no sign of elevated temperatures. The USGS also estimated that the soils in the tree-kill areas were releasing as much as 40 metric tons of CO_2 per hectare per day, which compares with typical CO_2 releases of 10 to 20 kilograms per hectare per day from normal forest soil.

Carbon dioxide was clearly a problem, but where was it coming from? A possible source was Mammoth Mountain itself, which last erupted about 500 years ago. More recently, a series of magnitude 6 earthquakes in 1980 was followed by swarms of temblors in 1983, 1989, and this year. Many volcanoes release large quantities of CO₂, but they do so at the summit and during periods of low-level eruptive activity. Mammoth, on the other hand, shows no signs of erupting.

A less likely source for the CO₂ releases was the soil. The soil of a healthy forest is enriched in CO₂ because of the



The tree-kill area near Horseshoe Lake (currently closed to campers). Other volcanoes in the world, such as Mt. Etna, release CO_2 when they are not erupting, but Mammoth is unique in the tree-kill associated with the releases.

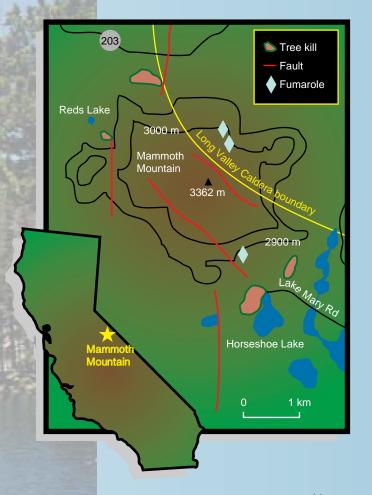
biological process of decomposition, which uses up oxygen and converts it to CO₂. But normal CO₂ enrichment is minor compared to the quantities found at Mammoth. Analysis of soil gas samples from areas of healthy forest indicated normal levels of biogenic CO₂. But in tree-kill areas and near the fumaroles, biogenic CO₂ made up only a tiny fraction of the total. So the most likely source for these anomalous CO₂ levels was indeed the mountain and volcanic activity deep inside.

At this point, the Livermore and Berkeley laboratories provided their expertise in gas analyses. Berkeley's analysis of carbon-13 and other gases in samples from tree-kill areas indicated "signatures" that were typical of magmatic ${\rm CO}_2$, signatures that were remarkably similar to those found at the fumarole where ${\rm CO}_2$ would be expected to be of magmatic origin.

Carbon-14 Clincher

Livermore's analyses of carbon-14 (14C), at its Center for Accelerator Mass Spectrometry, provided the clincher in determining the source of the CO₂. Mass spectrometry (MS) is a technique used to determine the mass of an atomic species or a molecular compound. Accelerator mass spectrometry (AMS), as it is applied at Livermore, adds three steps to MS. After the initial acceleration to kilovolt energies and the separation of the ion beam by mass, a second acceleration of millions of volts is applied. Then the ion beam is stripped to a charge state where at least three electrons are removed from the atoms of interest, which destroys all molecular species. Finally, the isotope has its mass, energy, velocity, and charge redundantly determined, which removes background interference. The resulting sensitivity is typically six orders of magnitude greater than that of conventional MS. AMS can find one atom of ¹⁴C in a trillion other carbon atoms.

In soil gas samples taken from healthy forest 1,500 meters from the nearest tree-kill area, Livermore scientists found that ¹⁴C levels were in keeping with those typically associated with



biogenic CO₂. Healthy forest soils have high levels of ¹⁴C because they are young. Volcanic magma, on the other hand, has been underground for millions of years and has no ¹⁴C.

The constant, predictable decay of ¹⁴C is what makes it an effective dating tool. Carbon-14 is a natural, radioactive carbon that is continuously produced in the upper atmosphere by cosmic-ray interactions. It is present in all green plants, which absorb it from the atmosphere. Through the food chain, all organisms ingest ¹⁴C over the course of their lives. Once an organism dies, it ceases to take in ¹⁴C, so the amount of ¹⁴C in its tissues steadily decreases. By measuring residual ¹⁴C with AMS, materials from 500 to 50,000 years old can be dated with remarkable precision.

An analysis of soil gas samples from the tree-kill areas showed extremely low ¹⁴C levels. In areas of apparently healthy forest, over 100 meters from the nearest dead or dying trees, ¹⁴C levels were only slightly higher. Carbon-14-free, magmatic CO₂ was apparently diluting the ¹⁴C in the soil.

Scientists now knew the source of the CO_2 . But they needed to verify that the CO_2 had made its way from the soil into the trees and that it was in fact CO_2 killing the trees. While some increase in CO_2 in the atmosphere is beneficial for trees, too much CO_2 in the soil is not. Livermore researchers analyzed pine needles for CO_2 content, and their data showed that the percent of magmatic carbon in needles from healthy forest was zero, in stressed trees it ranged from 2 to 6%, and in dead trees from two different areas it ranged from 2 to 65%. Generally, the more magmatic CO_2 a tree had absorbed, the

Just east of Yosemite National Park, California, Mammoth Mountain is at the southwestern edge of the 750,000-year-old Long Valley Caldera and at the southern end of the Inyo Craters volcanic chain. All four tree-kill areas are near faults on the flanks of Mammoth Mountain.

less healthy the tree appeared. Scientists believe that the $\rm CO_2$ inhibits the growth of tiny rootlets that normally absorb water and other nutrients from the soil; in other words, the $\rm CO_2$ is asphyxiating the trees.

This dilution of ¹⁴C has produced some startling apparent "ages." Analysis of ¹⁴C in a needle from a tree dead only a year showed an age of 7,200 years. The outer, most recent growth ring of a tree dead just a few years showed an apparent age of over 4,000 years, in contrast to its other recent rings, which showed modern ages.

Analysis of four tree cores indicates that in 1990 their ¹⁴C levels began to drop relative to modern ¹⁴C in the atmosphere, which is when dead trees were first noticed. By absorbing elements that can be "read" in their growth rings, trees are a unique recorder of historic activity.

Ongoing CO₂ and ¹⁴C Work

Scientists are using this experience at Mammoth to study historic activity at other volcanoes. Work is just beginning on research at Mt. Lassen, which last erupted from 1914 to 1916. Growth rings will be studied for anomalous CO₂ and ¹⁴C levels to determine whether a correlation exists between CO₂ levels and the eruption. Livermore researchers also hope to perform comparable studies at Mt. St. Helens and other modern volcanoes. Growth ring analysis of historic activity could prove to have enormous benefits for modern vulcanologists and others attempting to forecast volcanic eruptions.

Key Words: accelerator mass spectrometry, carbon-14, magmatic CO₂, volcanic activity.

Bibliography

C. D. Farrar, *et al.*, "Forest-Killing Diffuse CO₂ Emission at Mammoth Mountain as a Sign of Magmatic Unrest," *Nature*, **376**, 24 (August 1995).

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A Closer Look at Osteoporosis

ALF of all women born in this country will suffer a bone fracture because of osteoporosis. In osteoporosis, the bones become so fragile that they can break almost spontaneously. It is also true that more women die each year as a consequence of osteoporotic fracture than die of breast cancer. With numbers like these, the need to find a cure for osteoporosis is an urgent one.

Scientists at Lawrence Livermore National Laboratory are actively involved in this cause using the x-ray tomographic microscope (XTM) to produce three-dimensional images of bone. We are using these images to detect microscopic changes in bone structure of small laboratory animals and to study bone loss as well as increases in bone volume after treatment.

The only other method for producing accurate images of the microstructure of bone is sectioning, a time-consuming process that requires slicing the bone very thinly. This method destroys the sample and often introduces tiny pieces of debris, called artifacts, that can obscure important information. Furthermore, sectioning only produces two-dimensional images, which can be used to depict three-dimensional bone structure but not always with complete accuracy. XTM is the only method currently available for studying bone threedimensionally without destroying it. This means that studies can even be made in vivo.

The XTM at Work

The XTM was developed in 1991 as a spin-off of work on x-ray lasers for the Strategic Defense Initiative, and its inventors at LLNL and Sandia National Laboratories, Livermore, won an R&D 100 Award for the efforts. (See the October 1991 Energy & Technology Review for a detailed description of the XTM.) The XTM is a form of computed

The XTM consists of a source of parallel x rays, a rotary stage, an x-ray detector, and an analyzing computer. A specimen is mounted on the stage, and images are collected as the sample is rotated incrementally. These images are computationally assembled, through a procedure called Fourier-filtered back-projection, to construct single cross sections or three-dimensional images of the sample.

tomography, or CT, which was developed in the 1970s as a medical diagnostic tool. (The commonly used term "CAT scan" is a vestige of the earlier name "computerized axial tomography.") The LLNL configuration of the XTM is shown below.

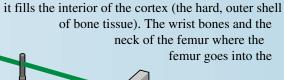
The XTM's spatial resolution is about 2 micrometers, shown at right. Using monochromatic (single-energy) synchrotron radiation at Stanford University's Synchrotron Radiation Laboratory (a part of the Stanford Linear Accelerator), the XTM can obtain spatial resolutions better than that of the best medical CT scanners. Monochromatic synchrotron radiation is used rather than conventional x rays; the former produces less distortion and, hence, better resolution because of its high brightness and the nearly parallel quality of its beam, known as collimation. The XTM is also superior to magnetic resonance imaging (MRI) because MRI cannot be used on metallic materials and because the resolution of the XTM is many times greater.

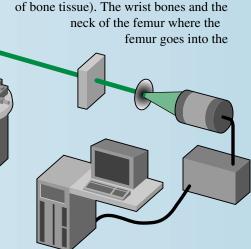
The XTM is excellent for nondestructive evaluation of a wide variety of industrial and military materials, but the radiation dose required to produce the XTM's high-resolution images currently limits its use in medical studies to laboratory animals or cadavers. Work continues to reduce the radiation exposure levels.

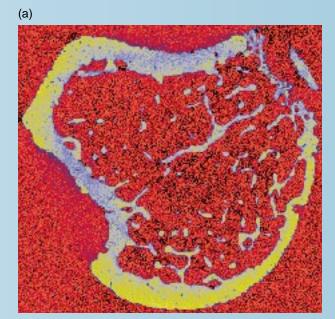
Searching for a Cure

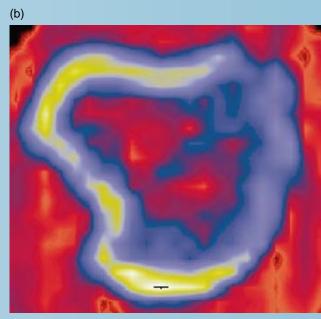
Researchers from the Laboratory and the University of California, San Francisco, are studying osteoporosis, looking at bone loss due to estrogen depletion and at potential treatments. The hope is to understand critical clinical time points in the development of osteoporosis to establish more effective interventions.

As with many studies of osteoporosis, our studies focus on trabecular bone, the sponge-like, connecting bone tissue that forms an internal supporting network mostly near joints where







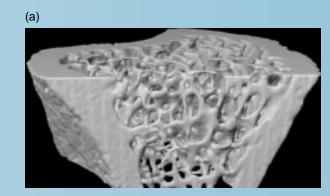


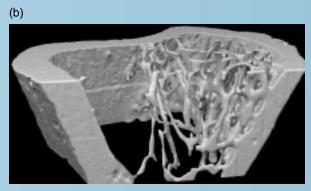
These figures compare (a) a two-dimensional XTM image of a rat's bone structure with (b) an image from a pQCT (Peripheral Quantitative CT) scanner, which is the highest resolution CT scanner commercially available for imaging biological structures.

hip joint have considerable trabecular bone; the vertebrae are almost entirely trabecular bone with very little cortex. Most osteoporotic fractures occur at these three sites.

Female laboratory rats are being used as subjects, half of which have had their ovaries removed to induce estrogen depletion. The non-ovariectomized rats serve as controls. Rats are excellent subjects for osteoporosis studies because estrogen depletion affects the bones of rats and humans in similar ways but much more quickly in rats than in humans.

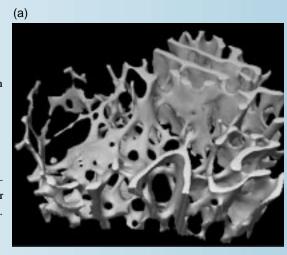
In the first study, we took XTM images of the rats' proximal tibias before their ovaries were removed, and again five weeks later to determine bone loss. (See images at right.) Trabecular bone volume decreased by approximately 60% in the estrogen-depleted animals compared to the control group. In addition, there was a significant change from an interconnected plate- and strut-like structure to one that was mostly disconnected struts. Dangling trabecular elements, supported only by marrow, were also seen in the ovariectomized animals. While these dangling elements contribute to total bone mass, they do not contribute to the stiffness or strength of the bone. We found that the number of trabecular interconnections decreased by 90% in the rats without ovaries compared to the control group. Combinations of broken trabecular struts and dangling elements most likely contribute to fracture risk.

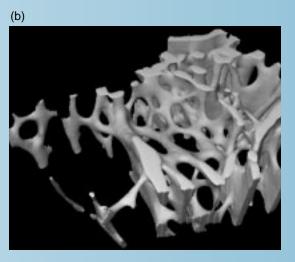




Three-dimensional composites of a rat's proximal tibia (a) just prior to ovariectomy and (b) 5 weeks after the ovariectomy, by which time estrogen depletion has caused osteoporosis

Representative XTM images (a) before ovariectomy and (b) 12 weeks after treatment with human parathyroid hormone (hPTH). The daily dose of hPTH was 400 micrograms per kilogram of body weight. Bone volume has been reestablished, but trabecular interconnections have not.





In our most recent study of a potential treatment for osteoporosis, ovariectomized rats were given various intermittent doses of human parathyroid hormone (hPTH) because it appears to be involved in the differentiation and regulation of bone morphogenic proteins. Scientists do not fully understand how these proteins work, but somehow they control the cells that make and resorb bone. Treatment with hPTH began 56 days after the rats' ovaries were removed and continued for four weeks. We found that hPTH did increase trabecular bone volume and trabecular thickness to baseline levels or higher, although it did not re-establish the bone's original structure by recreating lost trabecular interconnections. (See images above.) This and other studies suggest that hPTH's beneficial effects on bone mass do not depend upon the presence of functioning ovaries, which is very good news for post-menopausal women. The failure of hPTH to re-establish trabecular interconnections after 50% of them had been lost may mean either that earlier intervention or prolonged treatment, or both, are required.

Other Work with the XTM

Laboratory scientists also are working with Roche Biosciences of Switzerland to study bone loss caused by continuous use of steroidal anti-inflammatories such as prednisone. Preliminary work has demonstrated that the bone loss caused by medications such as prednisone is very different from estrogen-induced bone loss. Roche has developed a new compound that they believe prevents this bone loss.

We have also used the XTM to study periodontal disease and coronary artery disease. In the future, the XTM may be used to study fracture healing, kidney stone disease, autoimmune diseases such as arthritis, or any other calcified tissues. The key to all of this work is our ability to noninvasively examine body anatomy three dimensionally. With the XTM, we can evaluate therapies and conditions that affect many common but difficult-to-solve health problems. X-ray tomographic microscopy is significantly advancing our understanding of several very important public health issues.

Key Words: computed tomography, human parathyroid hormone, osteoporosis, steroidal anti-inflammatories, x-ray tomographic microscopy (XTM).

Bibliography

Kinney, J. H., *et al.*, "In Vivo, Three-Dimensional Microscopy of Trabecular Bone," *Journal of Bone and Mineral Research* **10**, 2 (1995).

Lane, N. E., *et al.*, "Intermittent Treatment with Human Parathyroid Hormone (hPTH[1–34]) Increased Trabecular Bone Volume but not Connectivity in Osteopenic Rats," *Journal of Bone and Mineral Research* **10**, 10 (1995).

"Nondestructive Imaging with the X-Ray Tomographic Microscope," *Energy & Technology Review*, UCRL-52000-91-9/10, Lawrence Livermore National Laboratory (September–October 1991) pp. 31–39.

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Abstracts

Theory and Modeling in Materials Science

A survey of four research projects shows how theory and modeling efforts by scientists in the Chemistry and Materials Science Directorate at LLNL are advancing our understanding of the property of materials with consideration of underlying structures. To account for radiation effects in some materials, we have created a hierarchy of simulation tools. Focusing on damage processes that occur when semiconductor devices are manufactured, we can now predict the distribution and growth of defects in silicon when dopant ions are implanted by a high-energy ion beam. Tantalum, a ductile metal with important defense applications, is the subject of another modeling project. Our recent model of deformation in tantalum uniquely accounts for its work-hardening behavior, and the same approach can potentially be applied to other types of commercially useful metals. In the area of energetic materials, we are simulating how a shock wave propagates through high explosives as a function of degradation, and we can predict how new explosives will perform under a variety of conditions. Finally, we have developed models that accurately mimic the complicated network and void structure of ultralow-density aerogels. Such models help us understand how molecules flow through aerogels and can facilitate the future use of these unconventional solids in applications that take advantage of their enormous surface area.

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LLNL and DOE Collaborate on Successful Fusion Facility Cleanup

Livermore and DOE's Oakland Operations Office teamed up to decontaminate, decommission, and close out—on time and under budget-the Ann Arbor Inertial Confinement Fusion Facility in Michigan. To execute the project, the Laboratory formed a team of hazardous waste management experts, a health physicist, industrial hygienists, hazards control technicians, and former KMS Fusion employees who were familiar with the building's past experimental processes. The major goals of the cleanup effort were to identify and remove the tritium; analyze and dispose of thousands of containers of chemicals (some radioactive); decontaminate and dispose of equipment; decontaminate the building; remove any other contaminated items; and return the cleaned building to its commercial owner for unrestricted use. They developed a waste sampling and analysis plan; characterized legacy waste (in drums generated during the facility's operation) and process waste generated from this project's activities; and after certification, packaged the waste for storage at the Nevada Test Site and DOE's Hanford, Washington, complex.

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